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Photon cross sections in the X-ray range present status

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Abstract : The present state of knowledge of photon cross sections in the energy range 1–100 keV is presented. Recent sources of experimental and theoretical data are given as well as other useful tools for the calculation of X-ray attenuation in matter.

Keywords : Photon cross sections, X-ray range, attenuation coefficients

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1. Introduction

Accurate X-ray attenuation coefficients are required in a variety of applications, X-ray diffraction (XRD), X-ray fluorescent analysis (XRF), electron microprobe analysis, proton-induced X-ray emission (PIXE) analysis, and radiography, to mention a few of them. A widespread discontent with the quality of compiled data caused the International Union of Crystallography (IUCr) to inaugurate a project aimed at improving the techniques for the measurement of attenuation coefficients and for producing better sets of tables for experimenters. Some results of the project have been published [1,2].

The status of photon cross section data was summarized by Hubbell [3] at the 2nd International Symposium on Radiation Physics (ISRP-2) in Penang, Malaysia. The purpose of the present work is to review some of the developments during the last decade and to point out useful tools for the calculation X-ray attenuation coefficients. Mass energy-transfer and mass energy-absorption coefficients, important for dosimetric applications, are not discussed in the present work. The reader is referred to a recent review and tabulation by Higgins *et al* [4].

2. Definitions

The linear attenuation coefficient, μ_1 describes the fractional reduction of the beam intensity, $-dI/I$, in a thin layer of thickness dx in an absorbing medium :

$$-\frac{dI}{I} = \mu_l \, dx \quad . \tag{1}$$

For a homogeneous medium, eq. (1) is readily integrated to give the well known Beer Lambert law :

$$I = I_0 \, e^{-\mu_l x} \tag{2}$$

where x is the thickness of a plane parallel layer which has surfaces normal to the beam direction, I_0 is the intensity of the incident beam and I is intensity of the emergent beam.

The mass attenuation coefficient, $\mu_m = \mu_l/\rho$, where ρ is the absorber density, is proportional to the total photon interaction cross section, σ, through the relation

$$\mu_m = \sigma \frac{N_A}{M} \tag{3}$$

where N_A is Avogadro's number and M is the atomic weight of the absorber material. In the energy range considered here, the total photon interaction cross section is generally given by

$$\sigma = \sigma_{pe} + \sigma_R + \sigma_C \tag{4}$$

where σ_{pe} is the photoeffect cross section, σ_R the Rayleigh (coherent) scattering cross section, and σ_C the Compton (incoherent) scattering cross section. Coherence in this context implies a fixed phase relationship between the incident and scattered waves for a single atom. Rayleigh scattering assumes an assembly of independent scattering atoms.

For a large perfect crystal *e.g.* a silicon single crystal, the coherent scattering is more complicated because of the cooperative solid-state effects of Laue-Bragg scattering (diffraction). The coherent scattering then consists of radiation channelled into directions given by Bragg's law as well as diffuse scattering due to the thermal vibration of the atoms. In this case, the total photon interaction cross section can be written

$$\sigma = \sigma_{pe} + \sigma_{LB} + \sigma_{TDS} + \sigma_C \tag{5a}$$

where σ_{LB} is the cross section of the Laue-Bragg scattering and σ_{TDS} is the cross section of the thermal diffuse scattering. Experimentally, it should be possible to choose a sufficiently narrow X-ray beam and an appropriate crystal orientation with respect to the incident beam direction, so that no Laue-Bragg scattering occurs. In such a case eq. (5a) reduces to

$$\sigma = \sigma_{pe} + \sigma_{TDS} + \sigma_C \quad . \tag{5b}$$

The photoeffect cross section is closely related to the anomalous dispersion correction in the forward scattering case. The scattering amplitude, f, of an isolated atom relative to that of a free electron is given by

$$f = f_0 + f' + if'' \, . \tag{6}$$

The first term, f_0, is the atomic form factor or the atomic scattering factor. The second and third terms are the anomalous dispersion corrections. The photoeffect cross section is proportional to the imaginary part of the dispersion correction at the photon energy E :

$$\sigma_{pe} = \frac{2hcr_e f''}{E} \tag{7}$$

where h is Planck's constant, c is the velocity of light, and r_e is the classical electron radius. It may be noted in passing that in practical units one has hc = 12.398 keV Å.

If the absorber is a chemical compound or a mixture, it is generally assumed that the contribution of each element to the attenuation is additive. It follows that the *rule of mixture* can predict the resulting attenuation properties of the material. The mass attenuation coefficient, for example, is given by

$$\mu_m = \sum w_i \left(\mu_m\right)_i \tag{8}$$

where w_i is the proportion by weight of the i'-th constituent. The mixture rule applied to μ_m is also called Bragg's rule.

Finally, it should be mentioned that the equations in this section refer to the 'narrow-beam' attenuation coefficient, *i.e.* it is assumed that the geometry of photon source, absorber and detector is such as to prevent any scattered photon, however small the scattering angle, from being detected. Departure from narrow-beam attenuation can arise in experimental situations.

3. Experiment

In quantitative analysis it would be desirable to know X-ray attenuation coefficients to within, say 3%. In order to discriminate between available theoretical data sets, it is necessary to compare them with experimental data that are accurate to within 1% or even better. Very few measurements published in the past fulfill this requirement. Experimental configurations and problems associated with the measurement of X-ray attenuation coefficients have been discussed by Creagh and Hubbell [1,2] and Creagh [5].

The existing experimental data situation for X-ray attenuation coefficients of the elements in the energy range from 0.1 to 100 keV has been amply reviewed by Hubbell *et al* [6], Solaman and Hubbell [7], Saloman *et al* [8] and Manson [9]. At the higher energies the experimental data are reasonably good. Thus in the energy range 10–100 keV the experimental data are in good agreement with each other and with theory. Exceptions are energy regions just above absorption edges, where larger discrepancies are noted. Experimental results for atoms with atomic number $Z < 4$ are questionable because of the very small cross sections involved. Impurity corrections nullify accurate measurements for these element and are important also in other low-Z absorbers. On the whole, the experimental data are reasonably satisfying also in the range 1–10 keV. This is true in particular for the medium

Z elements. It is surprising, however, to find that good experimental data are lacking for several elements [8].

The validity of the mixture rule is uncertain in the soft X-ray region generally, and close to absorption edges [10]. It has been estimated [11,12] that errors are generally less than 1 or 2 percent for photon energies 1 keV away from an absorption edge. However, recent experimental work [13,14] has shown that the range of non-validity of the mixture rule extends beyond 1 keV to, say about 1.5 keV above an absorption edge.

4. Theory

Computational developments have significantly improved the theoretical description of photon interactions with atoms. Calculations of photoeffect cross sections using relativistic wavefunctions have been reported, among others, by Cromer and Liberman [15,16], Storm and Israel [17] and Scofield [18], the latter reference being of particular interest in the present work.

Scofield [18] has calculated photoeffect cross sections using a model where the electrons are treated relativistically as moving in a Hartree-Slater central potential. For elements with atomic number from Z = 2 to 54, Scofield has provided correction factors for individual atomic subshells. Using these factors, the photoeffect cross sections can be renormalized so that they correspond to a relativistic Hartree-Fock model rather than the Hartree-Slater model used in the original calculation. The renormalization, which always is a decrease of the photoeffect cross section, has its greatest effect for outer shells.

Kissel *et al* [19] have developed a method for accurate evaluation of total-atom Rayleigh amplitude using the relativistic second-order S-matrix of quantum electrodynamics. The S-matrix formalism is considered the most rigorous method now available, even though it is difficult to program and costly in computer time. In practice, the contributions of the inner-shell electrons are calculated using the S-matrix formalism, and the contributions of outer-shell electrons are estimated using form-factor approximations [20]. Recent progress has produced new S-matrix results for scattering, beyond the impulse approximation and beyond the usual anomalous scattering factors [21].

Photoeffect cross sections can be obtained from the imaginary part of the S-matrix forward-scattering amplitudes using the optical theorem (cf. equation (7)). However, only a few sets of cross sections are at hand because of the considerable computing time needed for the calculations. Recently, Creagh and McAuley [22] have developed a model based on the use of relativistic Dirac-Slater wavefunctions. The Creagh and McAuley approach has been shown to give similar results to many S-matrix calculations [23].

5. Compilations

Tables of X-ray attenuation coefficients are purely theoretical, purely experimental or a mixture of theoretical and experimental information. Compilations that are widely used are for

example those produced by Storm and Israel [17], McMaster *et al* [24], Hubbell *et al* [25], Henke *et al* [26] and Hubbell [27]. A more exhaustive listing has been given by Creagh [23]. It may be noted that the tabulation of Hubbell [27] is based on the calculated photoeffect cross sections of Scofield [18] modified for $Z = 1$ to 54 using the relativistic Hartree-Fock renormalization factors supplied by Scofield [18].

Coherent (Rayleigh) scattering cross sections have been calculated and tabulated by Hubbell and Øverbø [28] using relativistic atomic form factors. The tables cover all elements and energies from 100 eV to 100 MeV. Similar tables of incoherent (Compton) scattering cross sections have been produced by Hubbell *et al* [29,30].

In practice it is not possible to meet all needs adequately by means of printed tables. Several authors [31–35] have derived formula which give a parametrization of the X-ray attenuation coefficient in appropriate ranges of energy and/or atomic number. Cromer [36] has made a Fortran program and a photoelectric cross section data file available for calculating anomalous scattering factors f' and f'' at arbitrary X-ray wavelengths. Output also includes the photoelectric mass absorption coefficient.

Berger and Hubbell [37] have developed a computer program which can be used to calculate, with a personal computer, photon cross sections for scattering, photoelectric absorption and pair production, as well as total attenuation coefficients in any element, compound or mixture, at energies from 1 keV to 100 GeV. The program, based on conclusions developed from comparisons with measurements in the Saloman, Hubbell and Scofield work [8], uses the unrenormalized Scofield photoeffect values. The official version of the program is available as XGAM from the NIST office of Standard Reference Data [38].

The new tables of X-ray attenuation coefficients in the International Tables for Crystallography, Vol. C (denoted by ITVC in the following) are based on a fully theoretical data set. The rationale underlying the production of the ITVC data set has been discussed by Creagh [23]. The data entries listed in ITVC agree with experimental and other theoretical values to better than 3% for most elements. Discrepancies of greater than 3% are most likely to occur for atomic numbers in the ranges $1 \leq Z \leq 4$ and $60 \leq Z \leq 90$.

The theoretical photoeffect cross sections used for the production of the ITVC data set are those of Creagh and McAuley [22]. The ITVC data are generally consistent with the unrenormalized Scofield calculation as shown by Gerward [39]. There is prefect agreement between the ITVC values and the unrenormalized Scofield values for the low- and medium-Z elements. For the lanthanides the agreement is better than 1.5%. Somewhat larger differences are found for the high-Z elements : general agreement to ±4% exists; however, differences up to 7% are observed for some entries.

6. Comparison between experimental and theoretical cross sections

In a critical analysis of soft X-ray cross sections data, Saloman and Hubbell [7] have compared experimental results with the Scofield photoeffect cross-sections with and without

renormalization. The authors conclude that the Scofield theoretical values, taken as a whole, are not improved by the Hartree-Slater to Hatree-Fock renormalization. Thus the unrenormalized results seem to agree better with the experimental results. There are exceptions, however, to the rule. Thus the results of the IUCr Attenuation Project have shown that carbon is an example in which the renormalization would improve the agreement between theory and experiment [2]. In the 10–100 keV range the effect of renormalization is only about 1% and no conclusion can yet be drawn about the value of renormalization in this decade [40].

Gerward [39,41] has suggested that the renormalized and the unrenormalized Scofield values satisfy the inequality

$$\sigma_{\mathrm{Sc,renorm}} < \sigma_{\mathrm{expmt}} < \sigma_{\mathrm{Sc,unrenorm}} \tag{9}$$

where σ_{expmt} is the experimental cross section and σ_{sc} is the Scofield value under consideration. In other words, it appears that the Scofield theoretical values with and without the Hartree-Slater to Hartree-Fock renormalization could be used as lower and upper limits to the experimental photoeffect cr sections.

The validity (or non-validity) of the mixture rule (8) has attracted a recent experimental interest [13,14]. In addition to the chemically-dependent fine structure (EXAFS) just above absorption edges, smooth monotonic curves drawn through this fine structure depart systematically from theory by as much as 10%. These systematic effects have been observed and discussed by Del Grande [42] and Del Grande *et al* [43].

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